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March 24, 2005

26th Compatibility, Aging, and Stockpile Stewardship
Aiken, SC, United States
April 26, 2005 through April 28, 2005

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Kinetic measurement and prediction of the hydrogen outgassing from the polycrystalline LiH/LiOH system.

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In this report, we present the use of temperature programmed reaction/decomposition (TPR) in the isoconversion mode to measure outgassing kinetics and to make kinetic prediction concerning hydrogen release from the polycrystalline LiH/LiOH system in the absence of any external H₂O source.

With TPR spectra obtained at greatly different heating rates, one can map out the variation in the activation energy of the process as a function of reacted fraction based on the following equation [1]:

$$\int_0^a \ln \left(\frac{da}{dT/\beta} \right) da = -\frac{E}{R} \int_0^a \frac{da}{T} + \int_0^a \ln(u f(a)) da \quad (1)$$

where t is time; α is the reacted fraction (0 to 1); u is the pre-exponential factor which includes many constants describing the initial state of the sample such as three dimensional shape factors of initial particles, molecular mass, density, stoichiometric factors of chemical reaction, active surface and number of lattice imperfections, and so forth; E is the activation energy for the rate controlling process, R is the gas molar constant, β is the heating rate, and $f(a)$ is an analytical function which is determined by the rate-limiting reaction mechanism.

The time at which a given conversion α is reached at an arbitrary temperature T_o , t_a , can be approximated by [2,3]:

$$t_a = \left[b \cdot e^{-\frac{E_a}{RT_o}} \right]^{-1} \frac{RT_a^2}{E_a} e^{-\frac{E_a}{RT_a}} \quad (2)$$

Here, T_α is the temperature corresponding to a given conversion α at the heating rate of β .

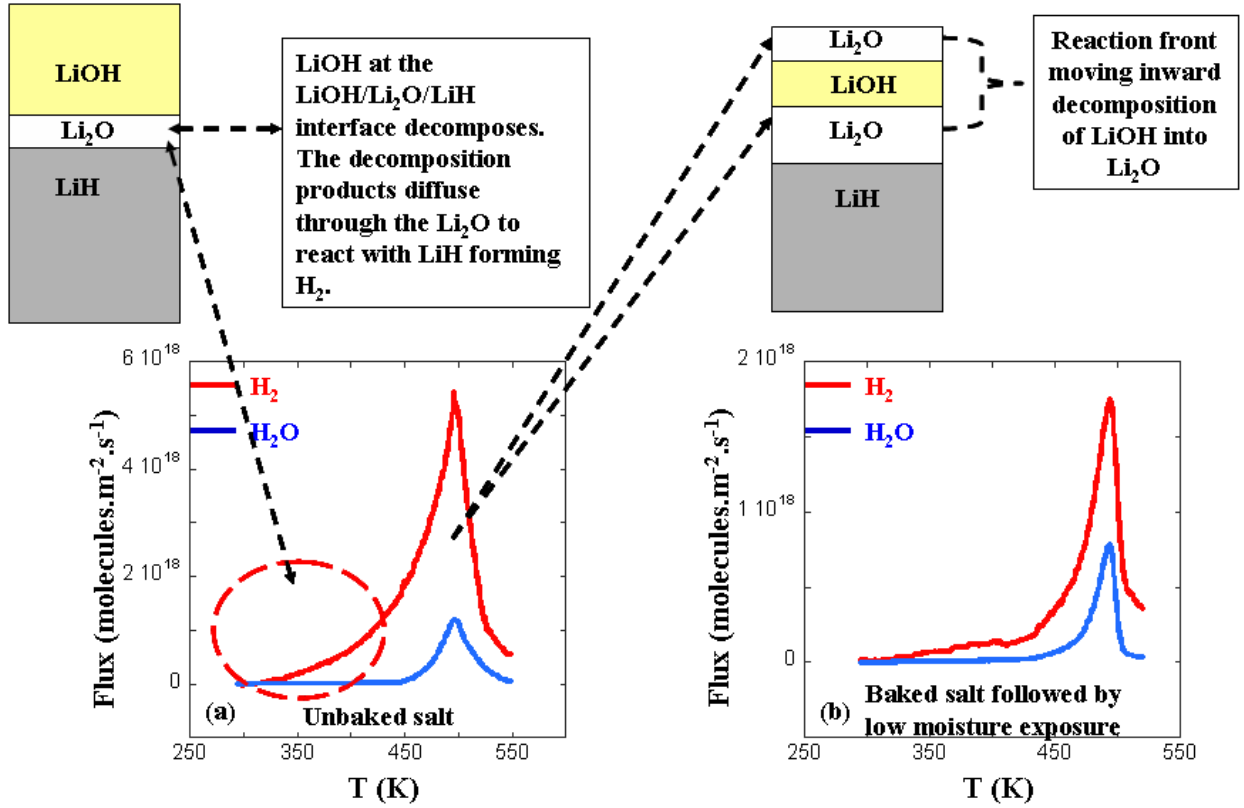


Fig. 1

In Fig. 1, we show the TPD spectra of unbaked salt (a) and baked salt followed by 30 ppm moisture exposure for 2.5 hours (b). Each TPD spectrum can be seen to compose of two separate reactions: (1) LiOH near the LiOH/Li₂O/LiH interface decomposes and the decomposition products diffuse through the Li₂O buffer layer to react with LiH and form hydrogen (lower temperature region in the TPD spectra where the H₂/H₂O signal ratio $\gg 10$); (2) the decomposition of LiOH from the surface inward [4-6] at higher temperature region to form Li₂O releasing H₂O, some of which proceeds toward the LiH substrate to react and form H₂. In a closed system containing LiH and LiOH, all H₂O generated from LiOH decomposition rapidly reacts with LiH to form H₂ [4]. Thus, in the absence of any external H₂O source, LiOH (in particular, interface/surface LiOH) is involved in all aspects of hydrogen outgassing from the

LiH/LiOH system. LiOH at interface and surface is under stress/strain (due to lattice, volume and density mismatch), often has fewer neighbors to bond to and so is expected to decompose more readily than LiOH in the bulk. This is probably the physical reason why the LiOH decomposition reaction has been experimentally found to advance from the interface/surface inward [4-6].

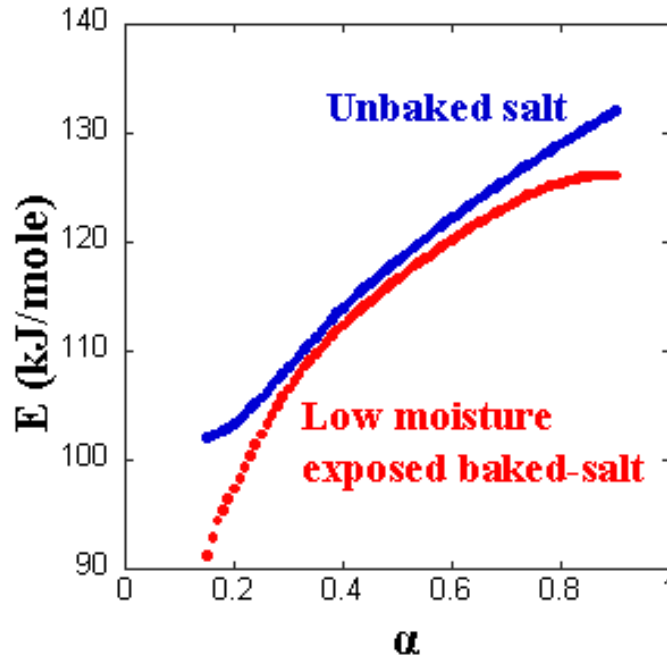


Fig. 2

In Fig. 2, we show the plots of E vs. α for unbaked salt (upper curve) and baked salt after 30 ppm moisture exposure for 2.5 hours (lower curve). It is observed that the decomposition process of LiOH in the LiH/LiOH system is a complicated process involving competing reactions with an overall activation energy barrier that increases with reacted fraction, α . The activation energy barrier for the hydrogen outgassing process in baked salt following low moisture exposure levels is observed to be much lower than that corresponding to an unbaked system. This can be understood by the following. Vacuum baking of the LiH/LiOH system at

high temperature converts LiOH into Li₂O with the formation of a large number of cracks in the Li₂O region to relieve stress [6-8]. Upon subsequent low moisture exposure for 2.5 hours, only a small population of Li₂O (more abundantly near interfaces and crack lines) is converted back to LiOH. The ratio of interface/surface LiOH to bulk LiOH is certainly much higher in baked system followed by low moisture exposure than in unbaked system, hence the inherent lower activation energy barrier for the decomposition of LiOH formed on baked salt at lower moisture exposure levels.

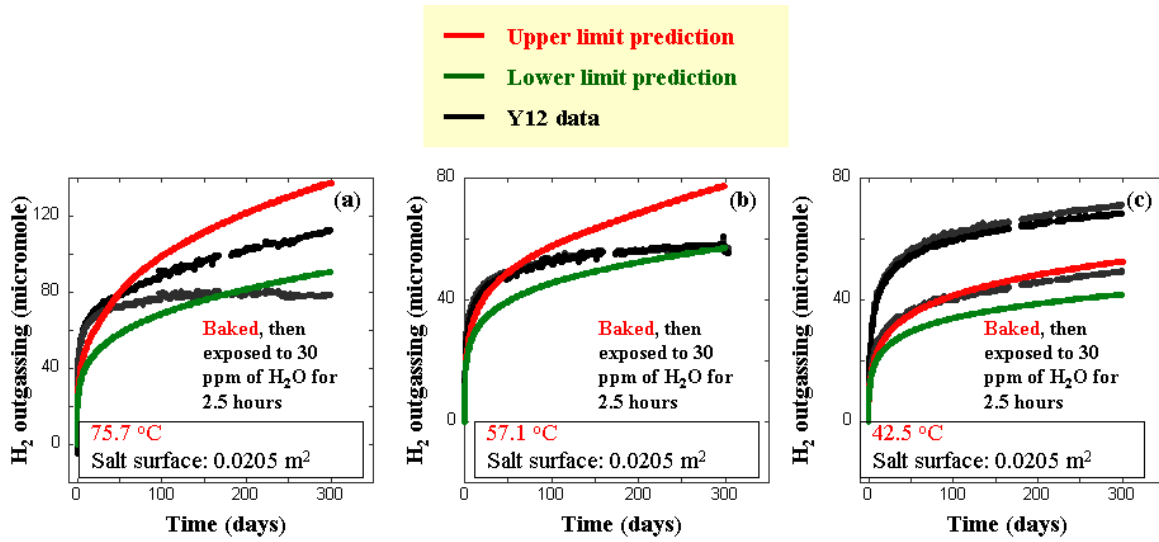


Fig. 3

In Fig. 3 (a), (b) and (c), we show comparisons between isothermal hydrogen outgassing data obtained by our collaborators at Y12 and outgassing prediction based on the model-free kinetics presented in Fig. 2 and equation (2) above. There are significant variations in the shapes and absolute values of the outgassing curves from Y12 (probably due to unavoidable sample to sample variation, assembly conditions and instrument response). With that taken into account, the agreement between our kinetic prediction based on TPD spectra according to the isoconversion method and isothermal outgassing data from Y12 is quite reasonable.

In summary, we have applied the technique of temperature programmed reaction/decomposition in combination with the isoconversion method of thermal analysis to obtain hydrogen outgassing kinetics and to make a kinetic prediction of the hydrogen outgassing from the polycrystalline LiH/LiOH system. The results of our kinetic prediction based on the model-free isoconversion technique agree fairly well with experimental isothermal outgassing data collected by our collaborators at Y12. In the course of this work, we have found that LiOH (in particular, interface/surface LiOH) is involved in all aspects of hydrogen outgassing from the LiH/LiOH system at temperatures below 550K in vacuum or dry environments.

This work was performed under the auspices of the U.S. Department of Energy, by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

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